

## On the potential of porphyrin-spiked triarylamine stars for bulk heterojunction solar cells†

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A novel porphyrin–triarylamine compound was synthesized to serve as a photosensitizer in bulk heterojunction solar cells (BHJ-OSCs). Based on cyclic voltammetric analysis, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the target porphyrin trimer were determined to be at  $-5.4$  and  $-3.5$  eV versus vacuum, respectively, and compared with those of other materials used for the construction of the BHJ-OSCs. Absorption and emission spectra of the film of the target porphyrin trimer were in good agreement with those of its solution. The charge transfer in a blended film of the porphyrin–triarylamine compound with phenyl- $C_{60}$ -butyric acid methyl ester (PCBM) was proven possible by photoluminescence measurements. The energy conversion efficiency of the BHJ-OSCs based on the target compound depended strongly on the donor : acceptor weight ratio and the thickness of the organic layer. Surface nanomorphologies of the films with different donor : acceptor ratios and thickness were investigated by atomic force microscopy (AFM). The short circuit current density ( $J_{sc}$ ) up to  $2.06$  mA cm<sup>-2</sup> was obtained from the BHJ-OSC fabricated herein.

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## Introduction

Unique potential advantages are associated with organic solar cells relating to the manufacture of flexible ultrathin devices *via* scalable and economically viable roll-to-roll fabrication.<sup>1</sup> Design of new materials for these devices requires large molar absorption coefficients, tunable electrochemical and photo-physical properties, and amenability to molecular modification. Efficiencies of new devices based on these materials have tended to increase steadily in the last decade, and porphyrins have emerged as valuable constituents in many bulk heterojunction organic (BHJ-OSC)<sup>2</sup> and dye-sensitized (DSSCs) solar cells.<sup>3</sup> Furthermore, porphyrins are also useful materials for photovoltaic cells,<sup>4</sup> organic light-emitting diodes (OLEDs),<sup>5</sup> and organic field-effect transistors (OFETs).<sup>6</sup>

Research by others, for example by Lindsey,<sup>7</sup> teaches how to use porphyrin macrocycles as light harvesting antennae by attaching them *via* their *meso*-carbons. Combinations of porphyrins with triarylamine units have also been explored,<sup>8</sup>

especially in the context of DSSCs. However, applications of these systems as photosensitizers in the BHJ-OSCs have been scarcely considered.

The work described here is unusual insofar as three porphyrins are connected to all three peripheral sites of a triarylamine core in a three-pointed star architecture through linear diphenylethynyl linkers. To the best of our knowledge, the porphyrin–triarylamine derivative with the proposed structure has not been studied as a basis for organic solar cells. However, this design combines the attributes of porphyrins as efficient light-absorbing groups with the properties of the triarylamine moiety that are favorable for hole transport. The triarylamine central unit is non-planar; therefore, we also anticipated that the solubility of the porphyrin/amine stars would be enhanced relative to similar systems that may be inclined to  $\pi$ -stack in the solid state; this effect might also reduce aggregation in solution. A similar observation was obtained from one of our recent studies on a porphyrin–triazine conjugate as a potential photosensitizer for the BHJ-OSCs.<sup>9</sup> Therefore, this work aims to demonstrate the synthesis, the investigation of photophysical and electrochemical properties, and the evaluation of the potential use for the BHJ-OSCs of this type of material.

## Results and discussion

## 1 Synthesis

The synthesis started from Lindsey's condensation<sup>10</sup> of benzaldehyde, pyrrole and 4-((trimethylsilyl)-ethynyl)benzaldehyde in

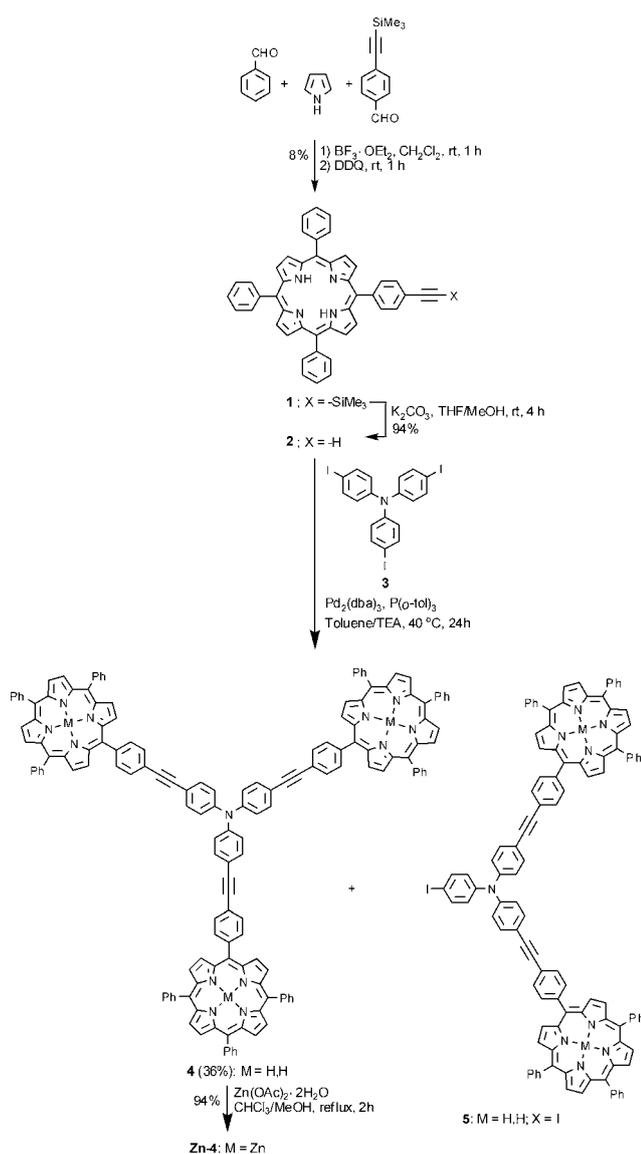
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the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  at room temperature for 1 h (Scheme 1). Then, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added to the reaction mixture as an oxidizing agent, leading to compound **1** in 8% yield. Based on thin layer chromatography (TLC), the cause of low yield is likely to be the competing polymerization of pyrrole and the formation of other statistically possible porphyrin by-products. In a  $^1\text{H}$ -nuclear magnetic resonance (NMR) spectrum of **1**, a characteristic inner proton peak of a free base porphyrin appeared as a singlet at  $\delta -2.25$  ppm. A singlet peak indicating a trimethylsilyl group was observed at 0.41 ppm. A trimethylsilyl group of compound **1** was readily removed by a reaction of **1** with  $\text{K}_2\text{CO}_3$  in tetrahydrofuran–methanol (3 : 1 v/v) at room temperature for 4 h, leading to compound **2** in 94% yield.<sup>11</sup> In the  $^1\text{H}$ -NMR spectrum of **2**, the singlet peak of a trimethylsilyl group at 0.41 ppm disappeared and a singlet peak of an ethynyl proton at 3.32 ppm appeared, indicating the successful deprotection of the trimethylsilyl group.



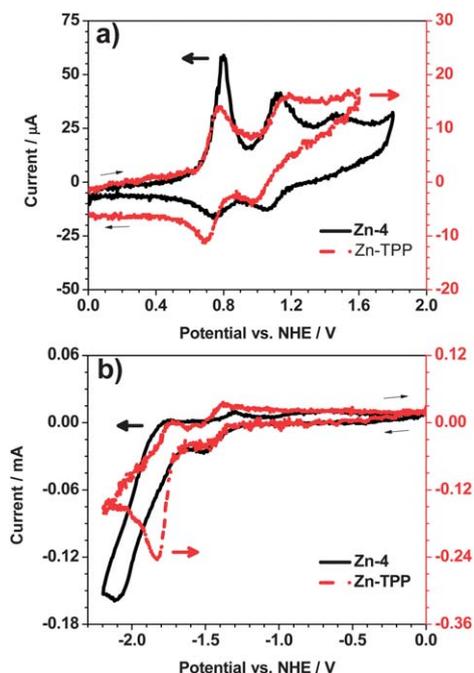
**Scheme 1** Synthesis of compound **Zn-4**.

Sonogashira coupling of compounds **2** and **3**<sup>12</sup> was performed under catalysis of tris(dibenzylideneacetone)dipalladium(0) and tri(*o*-tolyl)phosphine in toluene/triethylamine (TEA) under a nitrogen atmosphere at 40 °C for 24 h.<sup>13</sup> A three-column process was required to purify the target compound. The first silica column was used to remove unreacted compound **2** and other polar byproducts. After that, size-exclusion chromatography (SEC) was performed to separate compounds **4** and **5**. Finally, to get rid of possible impurities from SEC, the other silica column was employed. The desirable compound **4** was obtained in 36% yield, while compound **5** was collected in >90% purity according to thin layer chromatography (TLC) and NMR analysis. A mass spectrum of compound **4** showed a molecular ion peak at  $m/z$  2156.927, while that of compound **5** exhibited a molecular ion peak at  $m/z$  1645.721 and a  $(\text{M} - \text{I})^+$  fragment ion peak at  $m/z$  1519.852, resulting from the fragmentation of an iodine atom. After that, compound **4** was zinc-metallated in the presence of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in refluxing chloroform/methanol for 2 h, resulting in compound **Zn-4** in 94% yield. Upon the excitation at the maximum absorption, the emission of compound **4** appeared at 654 and 719 nm, while that of compound **Zn-4** was observed at 607 and 655 nm. The absence of the emission at 719 nm together with the disappearance of the singlet signal at  $-2.80$  ppm of the  $^1\text{H}$ -NMR spectrum of compound **Zn-4** indicated the complete metallation of the porphyrin ring. Satisfactory solubility of **Zn-4** in several common organic solvents, such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , toluene, chlorobenzene, and THF, allowed the preparation of the **Zn-4**-based BHJ-OSCs by our routine wet process using a concentration of **Zn-4** of up to 36  $\text{mg mL}^{-1}$ .

## 2 Electrochemistry

The redox properties of the **Zn-4** film were studied by means of cyclic voltammetry and compared with those obtained for a benchmark *meso*-tetraphenylporphinatozinc(II) (**Zn-TPP**) film. As shown in Fig. 1a, the electrochemical oxidation of the **Zn-4** film exhibited two reversible oxidation peaks at the oxidation peak potentials of +0.8 V and +1.1 V *versus* a normal hydrogen electrode (NHE), which can be attributed to the formation of radical cations and dication, respectively. A similar pattern was observed for the oxidation of **Zn-TPP**. The onset values of the first oxidation of both compounds were found to be equal, *i.e.* +0.7 eV *versus* NHE. The cyclic voltammograms recorded during the electrochemical reduction of **Zn-4** and **Zn-TPP** are presented in Fig. 1b. Two reversible peaks with the reduction peak potentials of  $-1.5$  and  $-2.1$  V *versus* NHE were observed, possibly caused by the formation of radical anions and dianions, respectively. The onset potential of the first reduction process was found to be  $-1.2$  V *versus* NHE, which is significantly lower than that of **Zn-TPP** ( $-1.4$  V *versus* NHE). This observation indicates the higher electronegative nature of **Zn-4** with respect to that of **Zn-TPP**.

The onset of the first oxidation and reduction potentials ( $E_{\text{ox}}$  and  $E_{\text{red}}$ , respectively), of **Zn-4** obtained from the cyclic voltammetric studies were used to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular



**Fig. 1** Cyclic voltammograms of **Zn-4** (solid line) and **Zn-TPP** (dashed line) films recorded during (a) oxidation and (b) reduction processes.

orbital (LUMO) energy levels ( $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , respectively) and the electrochemical energy gap ( $E_{\text{g}}$ ). The  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of **Zn-4** versus vacuum with an estimated energy of an NHE of  $-4.75$  eV versus vacuum<sup>14</sup> were approximated using the following equations:

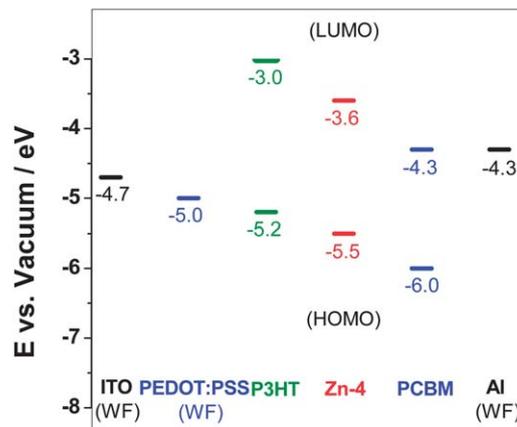
$$E_{\text{g}} = E_{\text{ox}} - E_{\text{red}};$$

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.75) \text{ (eV); and}$$

$$E_{\text{LUMO}} = -(E_{\text{red}} + 4.75) \text{ (eV)}^{15}.$$

According to the above equations, the resulting  $E_{\text{g}}$  of **Zn-4** was found to be 1.9 eV with  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of  $-5.5$  eV and  $-3.6$  eV, respectively. To determine whether **Zn-4** should be employed as a donor or acceptor in the BHJ-OSCs, the calculated energy levels were taken into consideration together with work functions (WFs) of ITO, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and Al, and the HOMO–LUMO levels of poly(3-hexylthiophene) (P3HT) and phenyl- $\text{C}_{61}$ -butyric acid methyl ester (PCBM) as illustrated in Fig. 2.

It should be noted that the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of PCBM and P3HT were obtained from the same cyclic voltammetry experiment conditions and calculations as those of **Zn-4** in order to minimize possible error due to the theoretical assumptions. The plot reveals that the LUMO level of **Zn-4** was positioned at the lower energy level than that of P3HT. Therefore, the electron transfer from the excited P3HT molecule to **Zn-4** and then further to the Al electrode should be thermodynamically allowed. At the same time, with the LUMO energy level of **Zn-4**



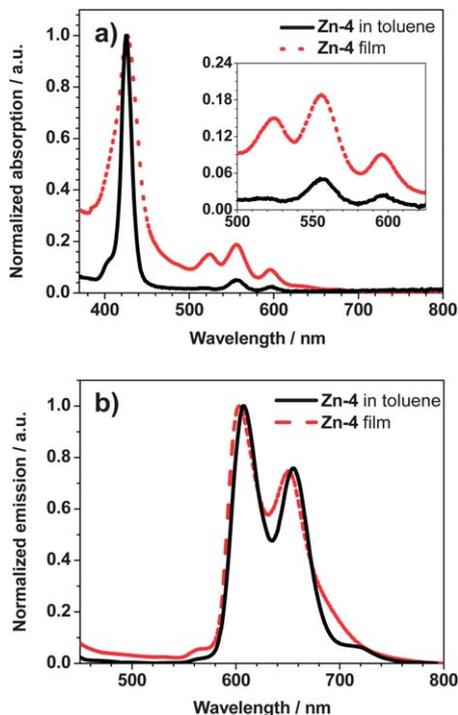
**Fig. 2** Comparative energy diagram of a possible **Zn-4**-based BHJ-OSC architecture.

located above that of PCBM and the HOMO energy level located below the WF of PEDOT:PSS, electron transfer from the excited **Zn-4** molecule to PCBM and the charge compensation from PEDOT:PSS to the HOMO of **Zn-4** should also be possible. Therefore, the use of **Zn-4** as an electron acceptor for P3HT and as a donor for PCBM in the BHJ-OSCs is further considered in the photoluminescence studies discussed below.

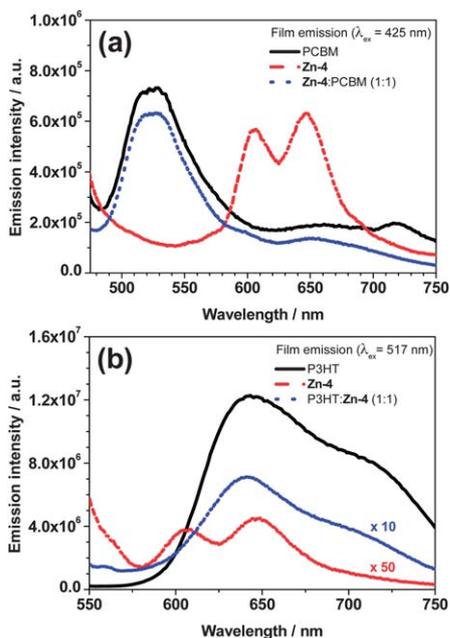
### 3 Photophysical properties and photoluminescence studies

The optical properties of **Zn-4** were studied by UV-vis spectrophotometry. A solution of **Zn-4** in toluene exhibited the characteristic absorption pattern of a Zn-chelated porphyrin having an intense B-band at 425 nm and Q-bands at 555 and 594 nm with absorption coefficients of  $6 \times 10^5$ ,  $3 \times 10^4$  and  $2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively (Fig. 3a). Broader peaks were observed in the absorption spectrum of the **Zn-4** film and were attributed to the aggregation of the macrocycle conjugation systems. An additional small peak at  $\sim 520$  nm was consistent with one of the characteristic absorption features that resulted from the formation of the porphyrin J-aggregates, which were intensively studied by Kano *et al.*<sup>16</sup> Upon excitation at 425 nm, the **Zn-4** solution in toluene and the **Zn-4** film gave similar emission patterns with peaks at  $\sim 600$  nm and  $\sim 650$  nm, as shown in Fig. 3b.

According to the electrochemical data described in the last section, **Zn-4** can be considered as both an acceptor for P3HT and a donor for PCBM in the BHJ-OSCs. To confirm the possibility of charge transfer between the donor and acceptor molecules in the blended films, a photoluminescence study of the films based on **Zn-4** and PCBM or P3HT was performed. The photoluminescence measurements were carried out by the photoexcitation of the **Zn-4**:PCBM (1 : 1 w/w) or P3HT:**Zn-4** (1 : 1 w/w) film at the maximum absorption of **Zn-4** (425 nm) or P3HT (517 nm, see ESI†), which served as the donor for each film, respectively. As shown in Fig. 4, complete quenching of the donor emission was observed in the **Zn-4**:PCBM film, indicating the occurrence of electron transfer from **Zn-4** to PCBM. However, the P3HT emission was not completely quenched by the presence of **Zn-4** in the P3HT:**Zn-4** film, suggesting the



**Fig. 3** (a) Absorption spectra of a solution of **Zn-4** in toluene (solid line) and a **Zn-4** film (dashed line). The inset shows a magnification of the region between 500 and 625 nm. (b) Photoemission spectra of a solution of **Zn-4** in toluene (solid line) and a **Zn-4** film (dashed line) upon photoexcitation at 425 nm.



**Fig. 4** Results of the photoluminescence studies of the (a) **Zn-4:PCBM** and (b) **P3HT:Zn-4** blended films.

inefficient donor–acceptor charge transfer in this blend. Therefore, the **Zn-4:PCBM** blended film was chosen as a photoactive layer in the BHJ-OSCs, whose fabrication and study are explained in the next section.

#### 4 Photovoltaic characteristics

In this study, we focus on the effect of the donor : acceptor ratio in the photoactive layer and the film thickness on the BHJ-OSC efficiency. The BHJ-OSC of interest consisted of a **Zn-4:PCBM** active layer sandwiched between a 60 nm PEDOT:PSS layer and a 150 nm Al top contact layer, all of which were patterned on an ITO-coated glass substrate. The weight ratio of **Zn-4:PCBM** was varied from 1 : 1 to 1 : 14 corresponding to the molar ratio from 0.388 : 1 to 0.028 : 1 (Table 1). Additionally, to confirm the results obtained from the above-mentioned photoluminescence studies, the BHJ-OSCs based on the P3HT:**Zn-4** blend with the weight ratios of 1 : 6, 1 : 1 and 6 : 1 were also prepared.

The results in Table 1 indicate the significant relationship between the **Zn-4:PCBM** weight ratio and the short circuit current density ( $J_{SC}$ ) of the devices. With the decrease in **Zn-4:PCBM** weight ratio from 1 : 1 to 1 : 6 (devices A–D),  $J_{SC}$  increased from 0.51 mA cm<sup>-2</sup> to 2.06 mA cm<sup>-2</sup>, indicating an optimum charge transfer when the PCBM proportion is higher within this range. However,  $J_{SC}$  dropped when the PCBM amount in the blended films was further increased to the **Zn-4:PCBM** weight ratio of 1 : 14 (devices E–H). All devices gave open circuit voltages ( $V_{OC}$ ) of 0.5–0.6 V and fill factors (FF) of 30–31%, with an exception for the device having the **Zn-4:PCBM** weight ratio of 1 : 1 that gave a relatively low FF compared to others, *i.e.* 26%. The optimum cell efficiency ( $\eta$ )

**Table 1** Current density–voltage characteristics of **Zn-4** based BHJ-OSCs

Device	Zn-4 : PCBM ratio		$J_{SC}/\text{mA cm}^{-2}$	$V_{OC}/\text{V}$	FF/%	$\eta/\%$
	By weight	By mol				
A	1 : 1	0.388 : 1	0.51	0.5	26	0.1
B	1 : 2	0.194 : 1	1.10	0.5	31	0.2
C	1 : 4	0.097 : 1	1.60	0.6	31	0.3
D	1 : 6 <sup>a</sup>	0.065 : 1	2.06	0.6	31	0.4
E	1 : 8	0.049 : 1	1.55	0.6	30	0.3
F	1 : 10	0.039 : 1	1.47	0.6	30	0.3
G	1 : 12	0.032 : 1	1.35	0.6	30	0.2
H	1 : 14	0.028 : 1	1.26	0.5	30	0.2
I	1 : 6 <sup>b</sup>	0.065 : 1	1.56	0.5	29	0.2
J	1 : 6 <sup>c</sup>	0.065 : 1	0.38	0.5	32	0.1
K	Zn-4			n/a <sup>d</sup>		
L	PCBM			n/a <sup>d</sup>		
P3HT : Zn-4 weight ratio						
M	1 : 6		0.01	0.2	27	<0.1
N	1 : 1		0.38	0.2	33	<0.1
O	6 : 1		0.03	0.1	24	<0.1
P3HT : PCBM weight ratio						
Standard	2 : 1		10.2	0.6	54	3.3

<sup>a</sup> A **Zn-4:PCBM** mixed solution was prepared from a 18 mg mL<sup>-1</sup> stock solution of each compound. <sup>b</sup> A **Zn-4:PCBM** mixed solution was prepared from a 9 mg mL<sup>-1</sup> stock solution of each compound. <sup>c</sup> A **Zn-4:PCBM** mixed solution was prepared from a 36 mg mL<sup>-1</sup> stock solution of each compound. <sup>d</sup> No significant  $J_{SC}$  and/or  $V_{OC}$  were measured.

of 0.4% was obtained from device D having the **Zn-4**:PCBM weight ratio of 1 : 6 with  $J_{SC}$  of  $2.06 \text{ mA cm}^{-2}$ ,  $V_{OC}$  of 0.6 V and FF of 31%.

In order to investigate the effect of the active layer thickness on our best solar cell having the **Zn-4**:PCBM weight ratio of 1 : 6, two additional cells with thicker and thinner **Zn-4**:PCBM films were fabricated. The thickness of the **Zn-4**:PCBM film of device D was roughly varied by the use of two times more diluted (device I) and concentrated (device J) **Zn-4**:PCBM mixed solutions compared to that employed in device D to prepare the active layer of the BHJ-OSCs. Device I exhibited  $J_{SC}$  and FF drops, while the major adverse change in device J was the decrease in  $J_{SC}$ , leading to lower  $\eta$  in both devices, compared to that of device D. From the atomic force microscopy (AFM) study, it was found that the active layers of devices D, I and J were very smooth with a root-mean-square (rms) roughness in the 0.36–0.45 nm range, and no distinctive feature like grains was observed, indicating a good blending of **Zn-4** and PCBM. However, the thickness of the active layers was found to be approximately 35, 70 and 160 nm for devices I, D and J, respectively. Therefore, it is likely that the very thin active layer in device I resulted in inefficient photon absorption, while device J might encounter a low charge dissociation rate and high charge recombination possibility due to its relatively thick active layer. The surface topographies of all the prepared **Zn-4**:PCBM films, with the **Zn-4**:PCBM ratios varying from 1 : 1 to 1 : 14, were very similar to that shown in Fig. 5.

As control experiments, devices K and L bearing pristine **Zn-4** and PCBM, respectively, as active layers were investigated. It was found that no significant current was detected for both devices, indicating that **Zn-4** and PCBM alone failed to serve as efficient photoactive compounds for such BHJ-OSCs. As regards the devices based on P3HT:**Zn-4**, the P3HT:**Zn-4** weight ratios of 1 : 6, 1 : 1 and 6 : 1 were used to prepare devices M, N and O, respectively. These devices exhibited low  $J_{SC}$  and  $V_{OC}$ , leading to low  $\eta$ , probably due to the poor donor–acceptor charge transfer as suggested by the above-mentioned photoluminescence study of the P3HT:**Zn-4** film.

Fig. 6a shows current density–voltage ( $J$ – $V$ ) curves of device D obtained from the measurements in the dark and under illumination. The dark curve shows diode

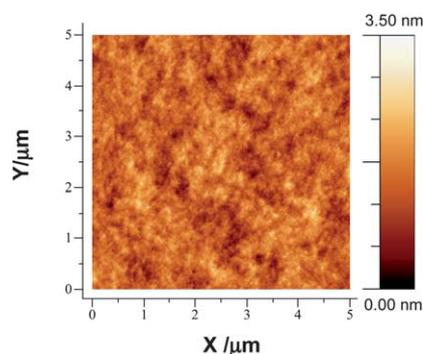


Fig. 5 An AFM image of the organic layer of device D.

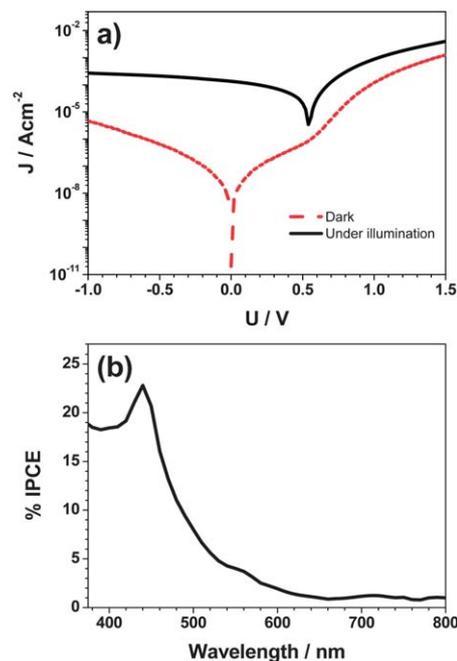


Fig. 6 (a)  $J$ – $V$  curve and (b) IPCE plot of device D.

performance with a rectification ratio of approximately 26, while the result obtained from the experiment under illumination indicates the photovoltaic effect with the enhanced current density and open circuit potential. The incident photon-to-current efficiency (IPCE) spectrum of device D is shown Fig. 6b. It exhibited the corresponding pattern to the absorption of **Zn-4** films with a maximum of 23% at a wavelength of 425 nm.

## Experimental section

### Materials and methods

All chemicals were of analytical grade, purchased from commercial suppliers and used as received without further purification.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were obtained in deuterated chloroform ( $\text{CDCl}_3$ ) using a NMR spectrometer operated at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  nuclei. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to the residual  $\text{CHCl}_3$  peak (7.26 ppm for  $^1\text{H-NMR}$  and 77.0 ppm for  $^{13}\text{C-NMR}$ ). Coupling constants ( $J$ ) are reported in hertz (Hz). Mass spectra were obtained by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) using dithranol as a matrix and electron spray ionization mass spectrometry (ESI-MS). Absorption and emission spectra of the solutions were measured in toluene at room temperature, and those of the films were obtained from the drop-cast films on a glass substrate. Absorption coefficients ( $\epsilon$ ) are expressed in  $\text{M}^{-1} \text{ cm}^{-1}$ .

### Non-commercial compound

Tris(4-iodophenyl)amine (**6**) was prepared according to the previously published literature.<sup>12</sup>

### 5,10,15-Triphenyl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (1)

Following a modified version of a previously published procedure,<sup>10</sup> a mixture of benzaldehyde (1.2695 g, 11.976 mmol), pyrrole (1.1721 g, 17.494 mmol) and 4-((trimethylsilyl)ethynyl)-benzaldehyde (0.8087 g, 3.998 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1600 mL) was stirred at room temperature until a homogeneous solution was obtained. BF<sub>3</sub>·OEt<sub>2</sub> (0.67 mL, 5.3 mmol) was then added to the solution and the reaction mixture was stirred at room temperature. After 1 h, 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) (2.7406 g, 12.073 mmol) was added and the reaction was continued for an additional 1 h. The resulting mixture was treated with triethylamine (0.8 mL) at room temperature for 5 min and then filtered through a silica pad (CH<sub>2</sub>Cl<sub>2</sub>). Then the solvent was removed and the crude product was purified by column chromatography [silica gel, ethyl acetate–hexanes (1 : 10)] to give the title compound as a purple solid (0.2367 g, 8%). <sup>1</sup>H-NMR δ –2.82 (s, 2H), 0.36 (s, 9H), 7.70–7.79 (m, 9H), 7.86 (d, *J* = 8.0 Hz, 2H), 8.15 (d, *J* = 8.1 Hz, 2H), 8.19 (d, *J* = 6.3 Hz, 6H), 8.78–8.86 (m, 8H); <sup>13</sup>C-NMR δ 0.2, 95.7, 105.2, 119.3, 120.4, 120.5, 122.7, 126.9, 127.9, 130.5, 130.7, 131.2, 134.6, 134.7, 142.3, 142.7; MALDI-TOF-MS *m/z* obsd 710.125; ESI-HRMS obsd 711.2943 ([M + H]<sup>+</sup>), calcd 711.2944 ([M + H]<sup>+</sup>, M = C<sub>49</sub>H<sub>38</sub>N<sub>4</sub>Si); λ<sub>abs</sub> 417, 513, 549, 593, 647 nm; λ<sub>em</sub> (λ<sub>ex</sub> = 417 nm) 659, 720 nm.

### 5,10,15-Triphenyl-20-(4-ethynylphenyl)porphyrin (2)

Following a modified version of a previously published procedure,<sup>11</sup> compound 1 (129.3 mg, 0.1819 mmol) in tetrahydrofuran–methanol (20.2 mL, 3 : 1) was treated with potassium carbonate (56.5 mg, 0.409 mmol) at room temperature. After 4 h, the solvent was removed under reduced pressure. The reaction mixture was then redissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organic phase was combined, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. After the removal of the solvent, the crude mixture was purified by a silica column [CH<sub>2</sub>Cl<sub>2</sub>–hexanes (1 : 3)], to obtain compound 2 as a purple solid (109.3 mg, 94%). <sup>1</sup>H-NMR δ –2.81 (s, 2H), 3.31 (s, 1H), 7.70–7.80 (m, 9H), 7.88 (d, *J* = 8.0 Hz, 2H), 8.15–8.23 (m, 8H), 8.79–8.87 (m, 8H); <sup>13</sup>C-NMR δ 30.2, 78.7, 84.2, 119.4, 120.8, 120.9, 122.1, 127.2, 128.2, 131.0, 131.5, 134.9, 135.0, 142.6, 143.3; MALDI-TOF-MS *m/z* obsd 638.227; ESI-HRMS obsd 639.2547 ([M + H]<sup>+</sup>), calcd 639.2549 ([M + H]<sup>+</sup>, M = C<sub>46</sub>H<sub>30</sub>N<sub>4</sub>); λ<sub>abs</sub> 417, 513, 549, 590, 647 nm; λ<sub>em</sub> (λ<sub>ex</sub> = 417 nm) 661, 720 nm.

### Compounds 4 and 5

Following a previously published procedure,<sup>13</sup> a mixture of compounds 2 (296.1 mg, 0.4636 mmol) and 3 (70.8 mg, 0.114 mmol) in toluene–TEA [5 : 1] (19.6 mL) was stirred under a nitrogen atmosphere until a homogeneous solution was obtained. After that, tris(dibenzylideneacetone) dipalladium(0) (19.0 mg, 0.0207 mmol) and tri(*o*-tolyl)phosphine (35.5 mg, 0.117 mmol) were added and the reaction mixture was stirred under a nitrogen atmosphere at 40 °C. After 24 h, the reaction mixture was filtered through a silica pad (toluene). After the

removal of solvent under reduced pressure, the resulting crude mixture was separated by a three-column process: a silica column [CH<sub>2</sub>Cl<sub>2</sub>–hexanes (1 : 1)], a size-exclusion column (tetrahydrofuran) and then a silica column [CH<sub>2</sub>Cl<sub>2</sub>–hexanes (1 : 1)] and triturated with hexanes to obtain compound 4 (88.6 mg, 36%) as magenta solids and a mixture containing 5 (22.6 mg, >90% purity). Compound 4: <sup>1</sup>H-NMR δ –2.80 (s, 6H), 7.58–7.98 (m, 45H), 8.11–8.52 (m, 24H), 8.74–9.12 (m, 24H); <sup>13</sup>C-NMR δ 29.6, 117.2, 118.4, 120.5, 124.4, 126.9, 127.9, 128.7, 129.3, 130.1, 130.3, 131.2, 133.3, 134.3, 134.7, 141.9, 142.3; MALDI-TOF-MS *m/z* obsd 2156.927, calcd avg. mass 2155.542 (M = C<sub>156</sub>H<sub>99</sub>N<sub>13</sub>); λ<sub>abs</sub> 420, 515, 550, 590, 647 nm; λ<sub>em</sub> (λ<sub>ex</sub> = 420 nm) 654, 719 nm. Compound 5: MALDI-TOF-MS *m/z* obsd 1519.852 [(M – I)<sup>+</sup>], 1645.721, calcd avg. mass 1644.698 (C<sub>110</sub>H<sub>70</sub>IN<sub>9</sub>).

### Compound Zn-4

Following a previously published procedure,<sup>11</sup> a solution of compound 4 (88.6 mg, 0.0411 mmol) in CHCl<sub>3</sub> (15.0 mL) was treated with a solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (364.8 mg, 1.662 mmol) in methanol (5.0 mL). After refluxing for 2 h, the reaction mixture was concentrated to dryness, redissolved in CH<sub>2</sub>Cl<sub>2</sub> and then washed with water. The organic phase was combined and dried over anhydrous MgSO<sub>4</sub>. After the removal of the solvent under reduced pressure, the crude product was purified by column chromatography [silica gel, CH<sub>2</sub>Cl<sub>2</sub>–hexanes (2 : 1)], to obtain compound Zn-4 as a magenta solid (90.7 mg, 94%). <sup>1</sup>H-NMR δ 7.66 (d, *J* = 8.4 Hz, 6H), 7.71–7.86 (m, 33H), 7.96 (d, *J* = 7.8 Hz, 6H), 8.18–8.30 (m, 24H), 8.93–9.03 (m, 24H); <sup>13</sup>C-NMR δ 89.5, 90.4, 118.2, 121.27, 121.34, 122.7, 124.3, 126.6, 127.5, 129.8, 131.7, 132.1, 132.2, 133.1, 134.4, 134.5, 142.8, 142.9, 146.9, 149.9, 150.2, 150.28, 150.31; MALDI-TOF-MS *m/z* obsd 2346.904, calcd avg. mass 2345.725 (C<sub>156</sub>H<sub>93</sub>N<sub>13</sub>Zn<sub>3</sub>); λ<sub>abs</sub> (ε) 425 (6 × 10<sup>5</sup>), 555 (3 × 10<sup>4</sup>), 594 (2 × 10<sup>4</sup>) nm; λ<sub>em</sub> (λ<sub>ex</sub> = 425 nm) 607, 655 nm.

### Electrochemical studies

The electrochemical properties of compound Zn-4 were determined by cyclic voltammetry in acetonitrile containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> by using an ITO-coated glass working electrode, a Pt wire counter electrode and a Ag/AgCl quasi-reference electrode (QRE) with a scan rate of 50 mV s<sup>–1</sup>. The Ag/AgCl quasi reference electrode was externally calibrated with a ferrocene/ferrocenium redox couple and a potential value of 0.40 V *versus* NHE was used. The value of the NHE *versus* vacuum level used in this work is –4.75 eV.<sup>14</sup>

### Photoluminescence studies

Stock solutions of Zn-4, P3HT and PCBM in chlorobenzene were prepared in the concentration of 18 mg mL<sup>–1</sup> and filtered through 0.45 mm PTFE syringe filters. The solution of Zn-4 was mixed with that of P3HT or PCBM in a weight ratio of 1 : 1. The resulting P3HT:Zn-4 and Zn-4:PCBM 1 : 1 (w/w) mixture was spin-coated on 15 mm × 15 mm glass substrates, which were cleaned by consecutive sonication in acetone, isopropanol and

deionized water, and then dried by purging with air, at 800 rpm for 25 s.

### Device fabrication and characterization

The above-mentioned stock solutions of **Zn-4**, P3HT and PCBM in chlorobenzene were used to prepare the mixed solution of **Zn-4**:PCBM with the weight ratio varying from 1 : 1 to 1 : 14 and that of P3HT:**Zn-4** with the weight ratios of 1 : 6, 1 : 1 and 6 : 1. The 15 mm × 15 mm ITO-coated glass substrates were first wiped with toluene and cleaned by consecutive sonication in acetone, isopropanol and deionized water, and then dried by purging with air. PEDOT/PSS solution (Heraeus Clevis™ P VP Al 4083) was spin-coated on top of ITO, followed by annealing at 150 °C for 10 min. After that, the organic mixed solution was spin-coated on top of this PEDOT/PSS layer. The resulting samples were dried under vacuum at ambient temperature for 1–2 h before a 150 nm thick Al top electrode was deposited by thermal evaporation in a vacuum of about 10<sup>-6</sup> mbar in a glovebox. The active area of the devices was between 6 and 10 mm<sup>2</sup>. The current–voltage (*I*–*V*) characteristics of the devices were measured in the dark and under simulated 100 mW cm<sup>-2</sup> AM 1.5 solar irradiation in a N<sub>2</sub> gas filled glovebox using a Keithley 236 source measurement unit. The intensity of the illumination was verified prior to each individual measurement using a calibrated silicon diode with known spectral response. Incident photon to current efficiency (IPCE) measurements were taken using a fiber optical light source from a 90 W xenon lamp, which is connected to a ACTON Spectra Pro150 monochromator and an EG & G 7260 DSP Lock-in amplifier to measure the current. Three to six samples for each cell condition were prepared to test the reproducibility and reliability of the results.

### Film morphology study

An atomic force microscope setup with a Digital Instruments Dimension 3100 (Veeco Metrology Group), working in tapping mode, was used in order to investigate the surface morphology and determine the thickness of the samples.<sup>17</sup>

## Conclusions

A novel soluble porphyrin derivative having three porphyrin macrocycles attached to the triarylamine central unit *via* the ethynylphenyl linkages (**Zn-4**) was successfully synthesized *via* three-fold copper-free Sonogashira coupling and characterized by spectroscopic techniques. According to cyclic voltammetry, the HOMO and LUMO energy levels of **Zn-4** were determined to be appropriate for possibly serving as both a donor and an acceptor for P3HT and PCBM, respectively, in the BHJ-OSCs. However, the photoluminescence studies of the P3HT:**Zn-4** and **Zn-4**:PCBM blended films and the characterization of the ITO/PEDOT:PSS/**Zn-4**:PCBM/Al and ITO/PEDOT:PSS/P3HT:**Zn-4**/Al solar cells showed that the charge transfer and photovoltaic effect were efficient when **Zn-4** served as a donor for PCBM. The energy conversion efficiency of the ITO/PEDOT:PSS/**Zn-4**:PCBM/Al solar cells was proven to be dependent on **Zn-4**:PCBM proportion and film thickness. Our best device exhibited an

energy conversion maximum efficiency of 0.4% with *J*<sub>SC</sub>, *V*<sub>OC</sub> and FF of 2.06 mA cm<sup>-2</sup>, 0.6 V and 31%, respectively. The outcome of this work should be a guideline for the modification of the device parameters based on this kind of material and/or the development of more complicated porphyrin–triarylamine conjugated systems like dendrimers, polymers or other hybrid networks with various chromophores.

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